



PATENT SPECIFICATION

609,945

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PROVISIONAL SPECIFICATION

Dyeing of Highly Polymeric Linear Esters

We, THOMAS VICKERSTAFF, of Hexagon House, Blackley, Manchester, a British Subject, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a Company incorporated under the laws of Great Britain, do hereby declare the nature of this invention to be as follows:—

10 This invention relates to the dyeing of highly polymeric linear esters more particularly the aromatic polyesters.

The aromatic polyesters with which the present invention is concerned are 15 the highly polymeric linear esters obtainable by heating glycols of the series $\text{HO}(\text{CH}_2)_n\text{OH}$, where n is an integer greater than 1 but not exceeding 10, with terephthalic acid or with an ester-forming derivative thereof, for 20 example, an aliphatic (including cycloaliphatic) or aryl ester or half-ester, an acid halide or an ammonium or amine salt, under conditions which yield the 25 esters in a highly polymerised condition.

Examples of such highly polymeric linear esters are those obtainable from terephthalic acid or an ester-forming derivative thereof and ethylene glycol, 30 trimethylene glycol, tetramethylene glycol, hexamethylene glycol and decamethylene glycol. These polyesters are high melting, difficultly soluble, colourless or substantially colourless materials 35 which can be formed into filaments which can be extended by drawing into strong flexible fibres showing, by characteristic X-ray patterns, molecular orientation along the fibre axis. Of 40 these polyesters, polyethylene terephthalate is preferred on account of its ready availability and of its outstanding utility as a textile material.

In general, these aromatic polyesters 45 have poor affinities for dyestuffs and they do not readily absorb aqueous liquids and, as a consequence, difficulties are experienced in satisfactorily dyeing them,

especially when in the form of highly oriented articles. 50

It has now been found that the aromatic polyesters may be satisfactorily dyed by means of fur dyestuffs.

According to the present invention there is provided a process for dyeing 55 aromatic polyesters of the kind hereinbefore specified which comprises dyeing said polyesters with fur dyestuffs in aqueous media.

The aromatic polyesters may be dyed 60 in the form of filaments, fibres, bristles, films, fabrics and like shaped articles which may or may not have been wholly or partly oriented by a cold drawing operation thereon. 65

The dyeing operation is effected by immersing the polyester in a solution containing a fur dyestuff and a solution containing a fur dyestuff developer. If 70 required the fur dyestuff and the fur dyestuff developer may be present in the same solution.

Suitable fur dyestuffs include for example those obtainable commercially under the name of Durafur Brown GM, 75 Durafur Brown M, Durafur Brown 2G, Durafur Brown R, Durafur Black R, Durafur Grey N and Durafur Grey BN.

Suitable fur dyestuff developers include for example those obtainable 80 commercially under the name of Durafur Developer C, Durafur Developer D and Durafur Developer E.

The dyestuff or the dyestuff developer may cause the fibre to swell during the 85 dyeing process. If required to facilitate the dyeing process, other swelling agents may be added to the solution or the polyester may be pretreated with additional swelling agents. Suitable additional 90 swelling agents include phenols, for example, phenol, *m*-cresol, *m*-methoxyphenol, β -naphthol, and catechol; amines, for example, α -naphthylamine, guanidine, aniline, and water-soluble 95 aniline salts; carboxylic acids, for

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and methacrylic acid; amides, for example, dimethylformamide, diethylformamide, dimethylacetamide, *p*-toluenesulphonamide and melamine; alcohols, for example, benzyl alcohol; ketones, for example acetophenone and cyclohexanone; nitriles, for example, glutaronitrile, adiponitrile, ethylene cyanhydrin, and lactonitrile; and other materials, for example, nitrobenzene, tetrachloroethane, tricresyl phosphate, and tetramethylsulphone. The swelling agent is conveniently dissolved or dispersed in water or an aqueous fluid and this solution or dispersion is used as a pretreating liquor, preferably at an elevated temperature, for example, at 90—100° C. If desired, the swelling agent may be incorporated in the dyeing liquor. Those of the above materials which are not soluble in water are con-

example, a salt of a long chain fatty alcohol sulphate.

The invention is illustrated but not limited by the following example in which the parts are by weight:—

EXAMPLE.

Polyethylene terephthalate yarn (100 parts) is immersed in a dyebath containing 4 parts of catechol and 3000 parts of water at 90° C. and is worked in the liquor for 20 minutes. The yarn is then lifted out of the bath and 2 parts of *p*-phenylenediamine dissolved in 200 parts of water is added. The yarn is immediately replaced in the bath and worked for a further ½ hour at 90° C. The yarn is then rinsed in cold water and dried. The yarn is coloured brown.

Dated the 26th day of March, 1946.

J. W. RIDSDALE,
Solicitor for the Applicants.

COMPLETE SPECIFICATION

Dyeing of Highly Polymeric Linear Esters

We, THOMAS VICKERSTAFF, of Hexagon House, Blackley, Manchester, a British Subject, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a Company incorporated under the laws of Great Britain, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the dyeing of highly polymeric linear esters more particularly the aromatic polyesters.

The aromatic polyesters with which the present invention is concerned are the highly polymeric linear esters obtainable by heating glycols of the series $\text{HO}(\text{CH}_2)_n\text{OH}$, where *n* is an integer greater than 1 but not exceeding 10, with terephthalic acid or with an ester-forming derivative thereof, for example, an aliphatic (including cycloaliphatic) or aryl ester or half-ester, an acid halide or an ammonium or amine salt, under conditions which yield the esters in a highly polymerised condition. Examples of such highly polymeric linear esters are those obtainable from terephthalic acid or an ester-forming derivative thereof and ethylene glycol, trimethylene glycol, tetramethylene glycol, hexamethylene glycol and decamethylene glycol. These polyesters are high melting, difficultly soluble, colourless or substantially colourless materials which can be formed into filaments

which can be extended by drawing into strong flexible fibres showing, by characteristic X-ray patterns, molecular orientation along the fibre axis. (Of these polyesters, polyethylene terephthalate is preferred on account of its ready availability and of its outstanding utility as a textile material.

In general, these aromatic polyesters have poor affinities for dyestuffs and they do not readily absorb aqueous liquids and, as a consequence, difficulties are experienced in satisfactorily dyeing them, especially when in the form of highly oriented articles.

It has now been found that the aromatic polyesters may be satisfactorily dyed by means of fur dyestuffs.

According to the present invention there is provided a process for dyeing aromatic polyesters of the kind hereinbefore specified which comprises dyeing said polyesters with fur dyestuffs as hereinafter defined in aqueous media.

By "fur dyestuffs" we mean the phenylene diamines and aminophenols which when applied to fur and subsequently oxidised give coloured derivatives on the fur.

The aromatic polyesters may be dyed in the form of filaments, fibres, bristles, films, fabrics and like shaped articles which may or may not have been wholly or partly oriented by a cold drawing operation thereon.

The dyeing operation is effected by immersing the polyester in a solution

containing a fur dyestuff and a solution containing a fur dyestuff developer. If required the fur dyestuff and the fur dyestuff developer may be present in the same solution.

Suitable fur dyestuffs include for example those obtainable commercially under the name of Durafur Brown GM, Durafur Brown M, Durafur Brown 2G, Durafur Brown R, Durafur Black R, Durafur Grey N and Durafur Grey BN.

Suitable fur dyestuff developers include for example those obtainable commercially under the name of Durafur Developer C, Durafur Developer D and Durafur Developer E.

The dyestuff or the dyestuff developer may cause the fibre to swell during the dyeing process. If required to facilitate the dyeing process, other swelling agents may be added to the solution or the polyester may be pretreated with additional swelling agents. Suitable additional swelling agents include phenols, for example, phenol, *m*-cresol, *m*-methoxyphenol, β -naphthol, and catechol; amines, for example, α -naphthylamine, guanidine, aniline, and water-soluble aniline salts; carboxylic acids, for example β -naphthoic acid, salicylic acid and methacrylic acid; amides, for example, dimethylformamide, diethylformamide, dimethylacetamide, *p*-toluenesulphonamide and melamine; alcohols, for example, benzyl alcohol; ketones, for example acetophenone and cyclohexanone; nitriles, for example, glutaronitrile, adiponitrile, ethylene cyanhydrin, and lactonitrile; and other materials, for example, nitrobenzene, tetrachloroethane, tricresyl phosphate, and tetramethylsulphone. The swelling agent is conveniently dissolved or dispersed in water or an aqueous fluid and this solution or dispersion is used as a pretreating liquor, preferably at an

elevated temperature, for example, at 90–100° C. If desired, the swelling agent may be incorporated in the dyeing liquor. Those of the above materials which are not soluble in water are conveniently dispersed with the help of, for example, a salt of a long chain fatty alcohol sulphate.

The invention is illustrated but not limited by the following example in which the parts are by weight:—

EXAMPLE.

Polyethylene terephthalate yarn (100 parts) is immersed in a dyebath containing 4 parts of catechol and 3000 parts of water at 90° C. and is worked in the liquor for 20 minutes. The yarn is then lifted out of the bath and 2 parts of *p*-phenylenediamine dissolved in 200 parts of water is added. The yarn is immediately replaced in the bath and worked for a further $\frac{1}{2}$ hour at 90° C. The yarn is then rinsed in cold water and dried. The yarn is coloured brown.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for dyeing an aromatic polyester of the kind hereinbefore specified which comprises dyeing said polyester with fur dyestuffs as hereinbefore defined in aqueous medium.
2. Process according to Claim 1 wherein the aromatic polyester is polyethylene terephthalate.
3. Process according to Claims 1 and 2 wherein there is present in the dyebath in addition to the fur dyestuff and fur dyestuff developer, one or more swelling agents for the aromatic polyester.

Dated the 30th day of May, 1947.

J. W. RIDSDALE,

Solicitor for the Applicants.

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THE PATENT OFFICE,

25, SOUTHAMPTON BUILDINGS,

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